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& AUTHOR(S)

Richard M. Osgood, Jr. and Robert Scarmozzino

7. PERFORMING CRGANIZATION NAMES) AND ADDRESS(ES)

Columbia University Microelectronics Sciences Laboratories 500 West 120th Street 1001 Schapiro CEPSR New York, NY 10027

& PERFORMING ORGANIZATION REPORT NUMBER

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9. SPCHSORING/MONITCHING AGENCY HAME(S) AND ADDRESSIES)

Dr. Jane Alexander DARPA/AFOSR 3701 N. Fairfax Drive 22203-1714 Arlington, VA

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This report summarizes a three-year research effort to explore advanced laser-chemical processing for microelectronics and integrated optics. The main goals of the work have been: a) to develop techniques for fabrication of integrated optical devices in GaAs multilayer and quantumwell structures, and b) to explore new and novel techniques of advanced semiconductor processing for microelectronics and optoelectronics.

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Richard M. Osgood, Jr.
Columbia University
Microelectronics Sciences Laboratories
500 West 120th Street
1001 Schapiro CEPSR
New York, NY 10027

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I. Introduction

A. Objective

This report summarizes a three-year research effort to explore advanced laser-chemical processing for microelectronics and integrated optics. The main goals of the work have been:

a) to develop techniques for fabrication of integrated optical devices in GaAs multilayer and quantum-well structures, and b) to explore new and novel techniques of advanced semiconductor processing for microelectronics and optoelectronics.

B. Overview

Section II of this report describes processing techniques developed for the fabrication of integrated optical and quantum-well devices. A key part of the program is the use of laser-induced photoelectrochemical etching to prototype waveguide-based devices, and this work is described here. Fundamental electrochemical studies related to this process are also described, as well as the application of the etching technique to multilayer heterostructure etching. For application to quantum-well and quantum-scale processing, we have developed a new technique for dry, low-damage, anisotropic etching of GaAs which is also described in this section. Finally, much of our work on integrated optics relies heavily on the ability to model these devices, and our efforts in this area are also discussed.

In Section III we discuss our work on developing new and novel techniques for advanced semiconductor processing. Various techniques for surface modification have been studied, including excimer laser deposition of cadmium for Cd/InP and Cd/InGaAs contacts, low-temperature oxidation/deoxidation of GaAs using an ECR plasma, and monolayer controlled

doping of GaAs by excimer laser zinc deposition and RTA diffusion. In addition, we have developed a technique for etching β -SiC, an important yet extremely difficult to process semiconductor material. Finally, we have developed a technique for etching through-wafer vias in SI-InP for application to low-inductance ground plane connections in microwave MESFET circuits.

In a small effort at the beginning of this contract, we have explored laser processing of polymer materials for applications in packaging. This work is described in Section IV.

Finally, details of the work summarized in Sections II-IV can be found in the attached publications.

II. Laser Processing Techniques for Fabrication of GaAs Integrated Optical and Quantumwell Heterostructure Devices

A. Fabrication of Integrated Optical Devices

In the previous contract we began using our capability for localized photoelectrochemical etching of GaAs to fabricate waveguides in heterostructure material for use in integrated optics. Several passive structures were fabricated as demonstrations of the potential of the technique, and several new device concepts were proposed. This preliminary work was continued in the early part of this contract and is summarized in Publications 1 and 11. This early work was demonstrative in nature, and it was necessary to also show that the process could be controlled sufficiently in order to produce low-loss single-mode devices useful for integrated optics. This was a key goal in the first half of this contract that has successfully been met.

A first step toward this goal was the refinement of our etching technique to allow high

resolution etching in the low-doped material required for low-loss waveguide devices. This entailed some basic electrochemical studies which are described in Section II.C. Having accomplished this process refinement, we set out to fabricate and characterize a variety of waveguides and waveguide components in terms of modal properties, loss, etc., as a function of various design parameters. In summary, we were able to produce low-loss (0.6 - 0.9 dB/cm), single-mode waveguides useful for prototyping integrated optical devices. In addition, we have fabricated low-loss building-block components such as bends, branches, couplers, etc., which are required in these circuits. This large body of work is described in detail in Publication 22.

Another key goal in this contract was to extend the range of this prototyping fabrication technique to the realm of active electro-optic devices. Toward this end, we first used a laser direct-write metallization technique developed in our laboratory to fabricate aluminum electrodes on our waveguides for the purpose of determining optimal waveguide geometry (see Publication 30). Our next step was to develop a metallization technique more suitable to our prototyping process which did not require the use of metallorganics and a vacuum chamber. Thus, we explored the use of laser direct-write patterning of photoresist, and were able to develop a process which allowed us to fabricate electrodes using laser patterning coupled with standard clean room techniques. This process was used to produce a polarization modulator, which coupled with an external polarizer formed an amplitude modulator. This device was tested and found to have a high extinction ratio (16dB) and low switching voltage (4V). This work is described in Publication 25.

Finally, we have begun to use our prototyping capability to fabricate new and novel integrated optical devices. The first is a channel-dropping filter proposed by H.A. Haus at

M.I.T. The device consists of two coupled waveguides, one of which has a grating with a quarter-wave step fabricated on top. This resonant DFB cavity produces resonant coupling of power from the transmission bus to the receiver arm with 50-100% efficiency, depending on the design. We have used our prototyping technique to fabricate the waveguides and waveguide components of the device. It was extremely useful to have this prototyping capability during the design stages as it allowed, for example, appropriate tailoring of the inter-waveguide coupling coefficient. The next step was to fabricate the gratings, and this was done in collaboration with P. Lin at Bellcore using e-beam writing. Our first device showed some promising resonant transfer peaks in the expected wavelength range, however, defective samples lead to an error in the coupling coefficients. A redesigned device has been fabricated and will be tested in the coming months.

In addition to the channel dropping filter, we are exploring other wavelength selective devices including wavelength demultiplexers. This work has entailed the use of holographic techniques to etch gratings controllably in n-GaAs. We have succeeded in reproducibly etching submicron gratings on the heterostructure facets of GaAs, including the waveguiding epilayer. We have demonstrated wavelength separation of multiplexed light travelling in the GaAs heterostructure. Further tests will include the integration of beam collimators into the chip and demonstration of demultiplexing of waveguided light.

B. Integrated Optical Device Modeling

An important capability that is required for doing integrated optical device work is the ability to accurately model the devices being fabricated. Therefore, we have developed several

analytical and numerical techniques that are appropriate to our structures. This work is described in Publications 5,8, and 19.

The numerical technique described in Publication 19 is particularly general, and applicable to other workers in the field. It is a propagating beam technique, which in principle, allows arbitrary types of geometry (although there are numerical restrictions). Unlike the typical FFT solution, however, our finite difference approach is much more stable, allowing for a significant increase in stepsize and corresponding reduction in computer time (see Publication 19 for details). We are currently using this technique to develop a general integrated optical device simulation package, B-PROP, which can be used by other researchers in the field. In particular, researchers at Allied Signal are very interested in this work.

C. Fundamental Electrochemical Studies of Light-Induced GaAs Etching

Because of its importance to our fabrication of integrated optical devices, we performed extensive work on microscopic photoelectrochemical etching with a close examination of factors which control the process physics. This exhaustive work, along with previous work in this area, was published in Publication 18.

A key result from these studies, as alluded to in Section II. A, was a refinement of our etching process to obtain high resolution in low-doped *n*-type GaAs material. Normally, the low doping degrades resolution through carrier diffusion. In our case, high resolution is accomplished through the use of appropriate solution chemistry yielding high surface reaction velocity, which removes the carriers before they have time to diffuse. This work is described in detail in Publication 20.

D. Laser Photoelectrochemical Etching of GaAs Multilaver Structures

Toward the end of the previous contract we had begun to explore the etching of multilayer structures using our photoelectrochemical etching process. We discovered an interesting and potentially useful effect, namely controlled undercutting of either GaAs or AlGaAs layers. This work continued under this contract, and we explored the effects of light intensity, solution composition, semiconductor doping, and multilayer thickness on the process. This work is described in Publication 4 and Presentation 24.

E. Low-Damage, Anisotropic Etching of GaAs for Application to MQW Devices

A difficult problem with the fabrication of many MQW devices is the etching of high aspect ratio structures without inducing damage to the delicate quantum layers. Typical reactive ion etching processes obtain the necessary anisotropy by applying a large bias voltage to induce etch directionality. This generates high energy ions which impact the sample and the sidewalls and induce damage in the material. Hence there is a need for a low-damage anisotropic etching technique for GaAs and related materials.

In this contract, we initiated a project to develop such a technique which was based on some fundamental observations in surface chemistry made elsewhere in our laboratory. The process uses a layer of Cl₂ condensed on the surface of GaAs at low temperature as the source of potentially reactive species. By irradiating the sample with patterned UV light from an excimer laser, the chlorine molecules are dissociated and the chlorine atoms react with the surface. The etch products are then dissociated by the laser pulse. The etch anisotropy results from the localization of reactive species to the surface in the irradiated zone. Since the process

is purely chemical in nature, no physical damage is expected.

During this contract we designed and constructed an etching apparatus, and demonstrated the technique. The process has been characterized as a function of key process parameters, and a model has been developed to explain the mechanism. This work is described in detail in Publications 31 and 33.

In addition, we have begun to apply the technique to real device problems. Patterned etching down to micron scale has been achieved using a gold mask and liftoff. This is currently being used to etch a QW laser structure. Testing of this device will occur in the coming months. Furthermore, silicon oxide and silicon nitride materials have been tested and work well as mask materials. These may be patterned to submicron dimensions using e-beam writing of photoresist. In the future we will test the limits of our technique using this approach.

III. New and Novel Techniques for Advanced Materials Processing

A. Excimer-Laser Deposited Cd/InP and Cd/InGaAs Contacts

The fact that most metal/InP and metal/In_{0.53}Ga_{0.47}As diode structures exhibit low Schottky barrier heights limits the application of these high performance optoelectronic materials. However, previous studies done by other workers have demonstrated that Cd contact metals provide high enough barriers to reduce diode leakage currents to levels acceptable for transistor operation. Such elevated height contacts are exceptional for these narrow band gap semiconductors, which form low barrier heights with more conventionally applied metals, yet are required for adequate noise margins and fan-out capability in MESFET circuits. Since

evaporation of Cd produces spatially non-uniform deposits incompatible with the fabrication of fine device features, there is a driving force for investigating alternative Cd deposition techniques. Previous work in our lab has shown that low resistivity Cd deposits exhibiting uniform coverage can be fabricated at room temperature by photodissociating the organometallic dimethylcadmium (DMCd) using either pulsed or cw lasers in the deep UV region of the spectrum. Accordingly, we have applied excimer laser photodeposition of Cd to the formation of Schottky barriers and micron-scale MESFETs on InP and In_{0.53}Ga_{0.47}As.

Current-voltage measurements of ideal Schottky diodes fabricated using this process yielded barrier heights of 0.70 eV and 0.55 eV to InP and $In_{0.53}Ga_{0.47}As$, respectively. These values are significantly higher than those characteristic of the Au/semiconductor diodes. Au/Cd/ $In_{0.53}Ga_{0.47}As$ transistors fabricated with this technique showed high transconductances (~200 mS/mm) and operating frequencies (f_{max} ~30 GHz), respectively. This work is described in detail in Publications 13 and 17.

B. ECR Surface Modification of GaAs by Low-Temperature Oxidation/Deoxidation

In the first phase of this work a custom-made electron cyclotron resonance (ECR) plasma source was added to our ultrahigh vacuum surface anal; sis system. The source was designed and built by Dr. William Holber, IBM, T.J. Watson Research Center, and Dr. John Forster, IBM General Technology Division. They were interested in collaborating with us since it offered them unique capabilities of investigating plasma interactions with surfaces which were not available to them at IBM. During the initial period we collaborated to characterize the properties of our ECR source.

Our first experiments investigated the use of hydrogen plasma, consisting chiefly of H atoms, to remove surface oxides on GaAs, with *in situ* XPS measurements. We have found that with appropriate exposure of the hydrogen plasma, both the As and Ga oxides can be completely removed, and a LEED image obtained, indicating that a clean, ordered surface can be achieved at room temperature with ECR hydrogen plasma processing. A technique like this can find its application for *in situ* low temperature clean surface preparation before MBE growth, or *in situ* passivation during device fabrication.

Subsequent to our experiments investigating the removal of oxides, we investigated the growth of oxide films on GaAs, the chemical structure of these oxides, and the oxide stoichiometry. Our results, in summary, are that an ECR plasma can effectively grow stoichiometric oxide on GaAs surface at room temperature. This oxide layer can be used as a sacrificial layer before MBE growth, and can be removed easily by hydrogen with the same plasma source. This ECR plasma grown oxide layer has also been recently shown useful as an effective Cl etching mask.

The above work is described in detail in Publications 21 and 27.

C. Monolayer-Controlled Doping of GaAs

The current, widely-applied techniques for doping selected areas of GaAs wafers are designed to achieve uniform lateral dopant densities over large areas. Recent work has shown, however, that laterally-graded dopant profiles can be used to optimize both electronic (GUNN diodes) and opto-electronic (graded index optics) device performance. Accordingly, an excimer laser-based doping process has been developed to accomplish uniform or graded diffusion

profiles. Specifically, low power 248-nm pulses from a KrF excimer laser are used to nonthermally photodeposit Zn from dimethylzinc (DMZn) onto selected GaAs surface regions. Finely-controlled uniform or graded Zn dopant source thicknesses are accomplished by controlling the number of pulses incident on a given area. Samples are then capped with Si₃N₄ and rapid thermal annealed to diffuse the source atoms into the underlying GaAs.

With the above technique, shallow uniform doping was obtained on the 1000-Å depth scale with concentrations up to 10^{20} /cm³. Spreading resistance measurements confirm that the Zn is activated as a p-type dopant.

To demonstrate laterally-graded diffusion profiles, a graded Zn source was photodeposited on GaAs substrates by irradiating the sample through a projection mask. By moving the mask in 1-mm increments and allowing increasing dwell times for a constant pulse rate, the total number of incident pulses was graded from 100-900 in increments of 100 pulses, yielding graded source thicknesses of ~ 3 to ~ 30 Å on 10-mm long samples. The resulting SIMS diffusion profiles show that the peak concentrations are graded across the surface in accordance with the thickness gradation of the Zn-source deposit. Thus it is demonstrated that graded-source thicknesses can be used to execute laterally-graded diffusions in a sample.

The above work is described in detail in Publication 26.

D. Photoelectrochemical Etching of β-SiC

This part of our laser microfabrication program is being cosponsored by Kulite Semiconductor, a NJ manufacturer of semiconductor sensors. SiC is currently under development at Kulite for high temperature pressure transducers. SiC is a useful material for

high temperature and high frequency applications due to its unique properties, such as its wide band-gap (2.2-3.2 eV), high melting point (2830°C) and high breakdown electric field $(4x10^6\text{V/cm})$. Good quality crystals were not available in the past, but recent advances in growth techniques have made α -SiC and β -SiC available in boule and epilayer form, respectively. This has led to the development of devices such as high temperature MOSFETs, high frequency diodes, and blue LED's. However, SiC is very inert, making patterning devices a difficult problem. Early in this project, SiC etching was identified as a critical area for sensor fabrication, since there has been heretofore no successful (i.e. workable) SiC etch. This need motivated a collaboration with Columbia University on the photoelectrochemical etching of SiC.

Under this contract, we have demonstrated an etching technique for β -SiC using a UV-laser. In addition, we have demonstrated several important results which are useful for the practical industrial application of this technique. These include large area etching using a UV lamp, mask-defined etching, and selective etching of n over p material for use as an etch stop. This work is described in detail in Publications 23 and 28.

E. Microwave Applications of Via Etching in SI-InP

Front to back interconnects in microwave structures are extremely important in order to improve performance at high frequencies. Such a structure significantly reduces parasitic inductance associated with microwave FET transistor leads, thus improving the gain and the overall performance of the circuit. Interconnects using via holes through the wafer provide the basis for such techniques, and have previously been demonstrated in GaAs. In July 1990, the Hughes Research Laboratory approached us to develop a technique for use in SI-InP, a very

important material for microwave applications. An important requirement was to obtain a higher aspect ratio geometry compared to what was previously obtained in GaAs (~ 1:1). As laser-induced photoelectrochemical etching was previously shown by us to produce very high aspect ratio structures, we investigated that approach for this application.

Under this contract we have developed a technique which can produce via holes with the required geometry in as little as 3-5 sec/via, and which terminate blindly at front side metallization. This meets all the practical requirements for the MESFET device applications. To develop this technique required exploration of a wide range of process parameters, such as solution, laser power, beam focusing, etc. In addition, several unique problems associated with high intensity etching in aqueous solution, such as bubble formation, had to be addressed.

We have also demonstrated that we can metallize these through-wafer vias using a simple electroplating scheme, and have obtained front to back resistance of 4Ω /via. Finally, we have demonstrated via fabrication on actual HEMT devices on an MMIC structure.

This work is described in detail in Publication 34.

IV. Laser Processing of Polyimide for Advanced Packaging

Under the previous contract, we initiated a collaboration with Honeywell to explore laser etching of polyimide, and demonstrated that a focused UV laser could produce localized thermal decomposition and etching of polymers. This work was completed under this contract, and is described in detail in Publication 2.

In addition, during this contract we explored techniques to deposit metal onto polymer

materials. In particular, we used our technique for direct patterning of aluminum metal to deposit metal lines on polyimide. An advantage of this technique is that it is low-temperature, and does not damage the polymer structure. This work is described in Publication 30.

Inventions

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- "Thin Film Magnetic Optical Isolator,"
 Miguel Levy, inventor.
 submitted to Columbia University, Office of Science and Technology Development
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- 2. R.M. Osgood, Jr., Laser-Surface Chemical Interactions and Applications, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany, June 15, 1989.
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- 11. Michael Schmidt, "Chemical Structure of the GaAs Oxide Formed by Deep Ultraviolet-Light-Enhanced Growth," Gordon Research Conference, Ventura, CA, February 26 -March 2, 1990.
- 12. Xiaoge Zhang, "Etch Rate and Feature Size in the Micrometer Scale, Laser-enhanced

- Aqueous Etching of III-V Semiconductors," Electrochemical Society Mtng., SOTAPOCS, Montreal, Canada, May 6-11, 1990.
- 13. Xiaoge Zhang, "Laser Electrochemical Etching of SiC," Electrochemical Society Mtng., SOTAPOCS, Montreal, Canada, May 6-11, 1990.
- 14. T.J. Licata, W.K. Chan, H. Schumacher, R. Bhat and R.M. Osgood, Jr., "DC and High Frequency of Performance of In_{0.53}Ga_{0.47}As MESFETs with Laser Deposited Gates," 48th Annual Device Research Conference, University of California, Santa Barbara, CA (June 25-27, 1990).
- 15. R.M. Osgood, Jr., "Laser-Fabrication for Integrated Electronics and Optics," OITDA Conference, Tokyo, Japan, (July 5-6, 1990).
- 16. R. M. Osgood, Jr., "Ultrasmall Photoelectrochemistry and its Applications for Electro-Optical Devices," ECS, Stevens Institute of Technology, Hoboken, NJ (September 26, 1990).
- 17. Michael T. Schmidt, "XPS Study of Compound Formation at Photodeposited Cd/InP and Cd/InGaAs Interfaces," presented at the American Vacuum Society Symposium, Toronto, Canada, October 8-12, 1990.
- 18. Zhong Lu, "XPS and LEED Investigation of the Renewal of GaAs-Oxide by Hydrogen ECR Plasma," presented at the American Vacuum Society Symposium, Toronto, Canada, October 8-12, 1990.
- 19. Robert Scarmozzino, "The CW Laser-Induced Dry Etching of GaAs and Related Substrates Using Reactive Methyl Groups from a DMZn Ambient," presented at the Materials Research Society Meeting, Boston, MA, November 26 December 3, 1990.
- 20. R.M. Osgood, Jr., "Advances in Laser Fabrication for Solid-State Electronics and Optics," presented for One Day Short Course, IBM, Thornwood, NY, February 8, 1991.
- 21. R.M. Osgood, Jr., "Laser Chemistry on Semiconductors for Application to Integrated Optics," presented at the Ontario Laser and Lightwave Research Centre, Toronto, Canada, February 26, 1991.
- 22. Joseph S. Shor, "Surface Micromachining of B-SiC Using Laser Assisted Photoelectrochemical Etching," 3rd International Conference on Amorphous and Crystalline SiC, Howard University, Washington, DC, April 11-13, 1990.
- 23. Joseph S. Shor, "Photoelectrochemical Etching of B-SiC," presented at the Electrochemical Society Meeting, Washington, DC, May 5-10, 1991.

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- 25. R.M. Osgood, Jr., "Laser-Fabricated Waveguiding Structures for Integrated Optic Circuits and Packaging," presented at the Optical Society of America CLEO (Conference on Lasers and Electro-optics), Baltimore, MD, May 12-17, 1991.
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- 31. Peiwen Li, "Electron Cyclotron Resonance Plasma Oxidation of SiGe Alloy, presented at the Materials Research Society Symposium, Boston, MA, December 2-6, 1991.
- 32. Zhong Lu, "Thermal Reaction of As₂O₅ with GaAs (110)," presented at the Materials Research Society Symposium, Boston, MA, December 2 6, 1991.
- 33. R.M. Osgood, Jr., "GaSb-oxide Removal and Surface Passivation Using Electron Cyclotron Resonance Hydrogen Plasma," PCSI-19 Conference, Death Valley, CA, January 28-30, 1992.
- 34. Wen Wang, "X-Ray Photoemission Study of GaSb Surface Cleaning by Electron Cyclotron Resonance Hydrogen Plasma," American Physical Society, Indianapolis, IN, March 16-20, 1992.
- 35. Louay Eldada, "Laser-Fabricated Electro-Optic Modulators in GaAs," Optical Society of America, New Orleans, LA, April 13-15, 1992.

- 36. R.M. Osgood, Jr., "Emerging Integrated Optics Program at Columbia," IBM, T. J. Watson Research Laboratory, Yorktown Heights, NY, April 27, 1992
- 37. Thomas Fink, "Electrochemical in-situ diagnostics for light-induced wet etching of multilayer structures," SOTAPOCS XVI, the Electrochemical Society Meeting, St. Louis, MO, May 17-21, 1992.
- 38. Michael B. Freiler, "Excimer Laser Driven Cryoetching of GaAs and Related Compounds," Gordon Research Conference, Meriden, New Hampshire, July 27-31, 1992.
- 39. Zhong Lu, "In Situ Surface Oxidation, Cleaning and Passivation of GaAs and GaSb using a Microwave Electron-Cyclotron-Resonance (ECR) Plasma Source," Gordon Research Conference, New Hampshire, August 10-14, 1992.

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